

GP 25988 (4)

# PATENT SPECIFICATION

(11) 1 422 057

1 422 057

- (21) Application No. 27094/73 (22) Filed 6 June 1973
- (31) Convention Application No. 56332/72
- (32) Filed 6 June 1972 in
- (33) Japan (JA)
- (44) Complete Specification published 21 Jan. 1976
- (51) INT CL<sup>2</sup> G03C 1/10; C07C 53/24; C07D 249/18; G03C 1/16, 1/18, 1/22, 1/24
- (52) Index at acceptance  
G2C C19E2A C19E4 C19G5 C19GX C19HX C19K7  
C2C 1452 20Y 213 226 246 250 252 25Y 292 29Y 30Y 366  
367 37X 628 67Y 69Y 77Y 798 79Y CM ZG



## (54) SPECTRALLY SENSITIZED SILVER HALIDE PHOTOSENSITIVE ELEMENTS

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami/Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a photosensitive silver halide composition containing at least 30 mole % of silver iodide and which is spectrally sensitized with an organic dye.

It is well known that a gelatino-silver halide photographic emulsion containing silver iodide in an amount below 30 mole % for example, such emulsions containing silver iodobromide, silver iodochlorobromide or silver iodochloride, can be spectrally sensitized by the use of sensitizing dyes, such as cyanine dyes, merocyanine dyes, rhodacyanine dyes, complex merocyanine dyes, styryl dyes and like methine dyes, in addition to organic dyes such as those described in "Cyanine Dyes and Related Compounds" by F. M. Hamer, published by Interscience Publishing Co. (1964).

It is also known that gelatino-silver halide photographic emulsions containing small amounts (<30 mole %) of silver iodide can be effectively sensitized by means of various chemical ripening treatments, including: sulphur sensitization with the use of sulphur-containing compounds such as aryl isothiocyanates, thiourea and sodium thiosulphate; reduction sensitization using reducing compounds such as hydrazine, stannous chloride and cystine; noble metal sensitization with the use of

## ERRATA

### SPECIFICATION No. 1,422,057

- Page 3, line 28, *for zoles) read zole)*
- Page 10, line 36, *after or insert a*
- Page 12, line 56, *for zylenol read xylenol*
- Page 13, line 4, *for butyl-2- read butyl-5-*
- Page 14, line 17, *for resnious read resinous*
- Page 18, line 1, *after of (first occurrence)*  
*insert a*
- Page 18, line 13, *for patterned read pattern*
- Page 21, Table 3 (continued), 2nd footnote,  
*for 49 ml. read 40 ml.*
- Page 23, line 17, *for optaionlly read*  
*optionally*
- Page 24, line 50, *for wherin read wherein*

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 1/18, 1/22, 1/24  
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It is also known that gelatino-silver halide photographic emulsions containing small amounts (<30 mole %) of silver iodide can be effectively sensitized by means of various chemical ripening treatments, including: sulphur sensitization with the use of sulphur-containing compounds such as aryl isothiocyanates, thiourea and sodium thiosulphate; reduction sensitization using reducing compounds such as hydrazine, stannous chloride and cystine; noble metal sensitization with the use of noble metal salts such as sodium aurous thiocyanate, potassium platinum tetrachloride, potassium iridium tetrachloride; and heavy metal sensitization with the use of heavy metal salts such as lead nitrate, cadmium chloride, thallium nitrate, as described in "The Theory of the Photographic Process", 3rd edition, edited by C. H. K. Mees & T. H. James, published by The Macmillan Co., N.Y., (1966). Sensitization is also effected by adding to a silver halide emulsion or developer liquid a compound such as lauryl pyridinium bromide, 1-phenyl-3-pyrazolidone, hydrazine sulphate or a polyalkylene oxide.

However, a silver iodide-containing photographic emulsion is known to have a somewhat inferior chemical ripening behaviour and to exhibit a relatively slow developing rate, as reported, for instance, in the "Journal of Photographic Science", vol. 8, pages 118—123, by E. A. Southern; the "Journal of Physical Chemistry", vol. 33, pages 864—872 (1929); *ibid*, pages 1583—1592 (1929) by F. E. E. German and D. K. Shen; and "Photographic Science and Engineering", Vol. 5, pages 216—218, by T. H. James, W. Vanselow and R. F. Quirk (1961), which literature also discloses useful conditions for forming such emulsions. In the case of sensitizing a silver iodide photographic emulsion, therefore, it is difficult to attain a desirably high sensitizing effect by simply applying known sensitizing techniques.

Moreover, unlike ordinary mixed silver halide particles which have a crystalline structure like that of rock salt, silver halide particles containing more than 30 mole % of silver iodide and are said to have a wurtzite structure or a zinc blende structure, so that it is impossible to form silver halide particles with a silver

SEE ERRATA SLIP ATTACHED

iodide content above 30 mole % having a rock salt structure by any conventional method employed for preparing mixed silver halide particles. This is true even if the molar ratio of the iodine ions used is increased.

Moreover, the photosensitive characteristics, for instance, sensitivity, ease of development and particularly the spectral sensitization of a silver halide containing above 30 mole %, preferably more than 40 mole %, of silver iodide is markedly different from that of other conventional mixed silver halides.

Thus a silver halide photographic emulsion containing at least 30 mole % silver iodide is endowed with only a minor spectral sensitivity by the use of a conventional methine type dye, which is in general effective for sensitizing a silver halide photographic emulsion containing less than 30 mole % silver iodide. For example, 3,3'-diethyl benzoxamonomethine bromide dye, 3,3'-diethyl benzoxadicyanone iodide and anhydro-3-(sulphopropyl)-4,5,4',5'-dibenzothia-9-ethyl-3'-(sulphopropyl)trimethine cyanine hydroxide show this effect; and the use of phenosafranine, which give a sensitizing effect to a silver iodobromide emulsion, results in a decrease in the sensitivity of a silver iodide photographic emulsion.

An object of this invention is to provide a silver halide photosensitive composition containing at least 30 mole % of silver iodide which has improved spectral sensitivity.

A photosensitive silver halide composition according to the invention comprises grains of photosensitive silver halide of which at least 30 mole % is silver iodide, and a spectrally sensitizing dye adsorbed on the surface of the silver halide grains, which sensitizing dye has an oxidation potential not exceeding 1.00 volt and a difference in values between its oxidation potential and its reduction potential of at least 2.00 volts (these values are expressed to two places of decimals).

The photosensitive silver halide composition of this invention which contains at least 30 mole % silver iodide has much improved stability as compared to compositions containing other mixed silver halide particles so that it is useful not only as (i) a gelatino photosensitive emulsion which forms images by a usual liquid developing procedure, but also as (ii) a heat-developable photosensitive element which forms images by a thermal developing procedure, and as (iii) a print-out photosensitive element which is directly recorded by radiation.

The primary feature of this invention resides in the use of the aforesaid sensitizing dye of the aforesaid potentials.

The reduction potential (Ered value) and the oxidation potential (Eox value) can be easily measured by those skilled in the art. The method of measurement is described and reported in various literature and reports, e.g., "Naturwissenschaften" Vol. 47, pages 353 and 512, by Astanienda, 1960; "New Instrumental Methods in Electrochemistry" by P. Delahay, published by Interscience Publishers Co., 1954; and "Polarographic Techniques", 2nd Edition, by L. Meites, published by Interscience Publishers Co., 1965.

The Ered value defines the electric potential at which the compound is reduced by the injection of an electron at the cathode in voltammetry, and it is considered to primarily and approximately correlate with an excited energy level of the compound.

The Eox value defines the electric potential at which an electron is ejected at the anode in voltammetry, and it primarily correlates with the maximum electron energy level occupied at the normal state of the compound.

As used in the invention the Ered value is determined by obtaining an electric voltage-current curve using tetra-*n*-propyl ammonium perchlorate as the supporting electrolyte (in a solution in acetonitrile of  $1 \times 10^{-4}$  to  $1 \times 10^{-6}$  moles per litre of the compound to be measured) and by using a mercury dropping electrode at 25°C while taking SCE (standard Calomel electrode) as the reference electrode, and thereafter obtaining the half-wave potential from the previously obtained voltage-current curve. The Eox value is determined likewise except for using sodium perchlorate as the supporting electrolyte in combination with a rotary platinum electrode.

A series of Ered and Eox values measured will permit the correction of any deviation at a maximum of approximately 100 millivolts due to the influence of liquid-to-liquid contact electric potential, imperfections in the correction of the liquid resistance of the sample solution, hindrance by the effect of the anion of sensitizing dye and the influence of dye concentration. Such deviation may also be corrected for by taking 3,3'-diethyl thiocarbocyanine perchlorate as a standard sample so as to ensure the reproducibility of the value of the potential to be measured.

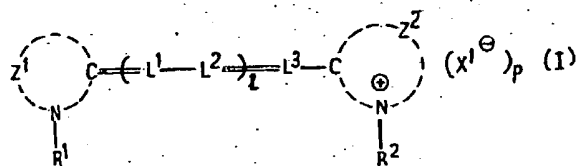
The dye used in accordance with the present invention must have an Eox value not exceeding 1.00 volts and have a difference between the Eox and Ered values at least 2.00 volts, and should preferably fall inside the region designated "zone I" shown in Figure 1 of the accompanying drawings, which is a graph of oxidation and reduction potentials showing regions which are referred to as zones I, II and III according to the values of Eox and Ered in volts.

A preferred minimum Eox value is more than 0.00 volt, and a preferred maximum Ered value is 3.00 volts.

The sensitizing dyes used in the present invention are most preferably sensitizing non-methine or (poly) methine dyes, i.e. one without any methine bridge between the two halves of the molecule or with more than one methine group in such bridge and especially cyanine dyes, which are usually merocyanine dyes or hemicyanine dyes. Many Examples of such dyes are given in the aforesaid "The Theory of the Photographic Process" at pp. 201—232 (the section: "Cyanine and Related Dyes").

Preferred classes of such sensitizing dyes used in the present invention are those represented by the following general formulae (I), (II) and (III).

*General Formula I:*



In the above general formula (I):

Z¹ and Z² each represent the atoms necessary to form a five- or six- membered nitrogen-containing heterocyclic nucleus, oxazole, naphthoxazole, thiazole, benzthiazole, selenazole, naphthoselenazole, imidazole, benzimidazole, naphthimidazole, pyridine, indolenine and quinoline nuclei, which may be substituted.

Preferred examples of heterocyclic nuclei containing Z¹ or Z² are oxazole nuclei (e.g., phenylbenzoxazoles (e.g., 5-phenyl benzoxazole), halogenbenzoxazoles (e.g., 5-chlorobenzoxazole or 5-bromobenzoxazole), alkylbenzoxazoles (e.g., 6-methyl or 5-methylbenzoxazole), alkoxybenzoxazoles (e.g., 5-methoxybenzoxazoles), hydroxybenzoxazoles (e.g., 5-hydroxybenzoxazole), alkoxycarbonylbenzoxazoles (e.g., methoxycarbonyl benzoxazole), carboxybenzoxazole, naphthoxazoles, (e.g., 6,7-dihydroxy-naphthoxazole), indolenines (e.g., 1,1-dimethyl indolenine), thiazole nuclei e.g., halogenbenzothiazoles (e.g., 5-chlorobenzothiazole), alkylbenzothiazoles (e.g., 5-methylbenzothiazole), naphthothiazoles, phenylthiazoles (e.g., 5-phenylthiazole), alkoxythiazoles (e.g., 5-methoxythiazole), selenazole nuclei (e.g., benzoselenazole, alkylbenzoselenazoles (e.g., 5-methylbenzoselenazole), naphthoselenazole), imidazole nuclei, e.g., cyanobenzimidazoles (e.g., 5-cyanobenzimidazole), trifluoromethylbenzimidazoles (e.g., 5-trifluoromethylbenzimidazole), halogenbenzimidazoles (e.g., 5,6-dichlorobenzimidazole, 5-trifluoromethyl-6-chlorobenzimidazole), benzimidazole, alkoxycarbonyl benzimidazoles (e.g., 5-methoxycarbonyl benzimidazole), alkyl sulphamoyl benzimidazoles (e.g., 5-methyl sulphamoyl benzimidazole), morpholinosulphobenzimidazole (e.g., 5-morpholinosulpho-6-chloro-benzimidazole), alkylcarbamoylbenzimidazoles (e.g., 5-methyl carbamoyl benzimidazole), naphthimidazole, pyridines, alkylquinolines (e.g., 6-methylquinoline) and alkoxyquinolines (e.g., 6-methoxy-quinoline).

L¹, L² and L³ each represents an optionally substituted methine group, for example those methine groups substituted with an alkyl group (e.g., methyl, ethyl or propyl group), a halogen atom (e.g., chlorine), an alkoxy group (e.g., methoxy) or a phenyl group.

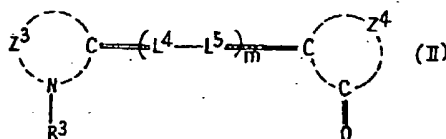
R¹ and R² each represents an optionally substituted alkyl or aryl group. The alkyl group preferably has 1 to 4 carbon atoms, e.g., methyl, ethyl, propyl, butyl or isobutyl, and may be substituted alkyl such as hydroxyalkyl groups (e.g., hydroxyethyl or hydroxymethyl), carboxyalkyl groups (e.g., 3-carboxypropyl or 3-carboxybutyl), sulphaalkyl groups (e.g., sulphopropyl or 4-sulphobutyl), sulphaalkoxyalkyl groups (e.g., 2-(3-sulphopropoxy)ethyl or 2-[2-(3-sulphopropoxy)ethoxy]ethyl), aminoalkyl groups (e.g., sulphopropyl aminoethyl or dimethyl aminoethyl), aralkyl groups wherein the aryl moiety contains a benzene

ring (e.g., benzyl or *p*-methyl benzyl), cyanoalkyl groups (e.g., cyano-propyl), carbamoyl alkyl groups (e.g., morpholinocarbamoyl ethyl) or allyl. The aryl groups preferably contain a benzene ring (e.g., phenyl and *p*-sulphophenyl groups).

$X^1$  represents an anion forming a salt with a nitrogen cation included in the cyanine dyes, such as a halogen anion (e.g., iodide or bromide), or organic acid anion (e.g., *p*-toluene sulphonate or ethyl sulphate) or mineral acid anion (e.g., perchlorate ion).

$l$  is the number 0 or 1;  $p$  is 0 or 1 but is 1 when the dye forms a betaine-like intermolecular salt.

General formula II:



In the above general formula (II):

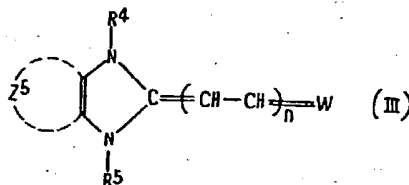
$Z^3$  represents the atoms needed to form a five- or six-membered nitrogen-containing heterocyclic nucleus. Examples of such heterocyclic nuclei include thiazole nuclei [e.g., phenyl thiazole (e.g., 4-phenyl thiazole), benzothiazole, alkyl benzothiazoles (e.g., 5-methyl-benzothiazole)], thiazoline nuclei, oxazole nuclei [e.g., benzoxazole, halogeno-benzoxazoles (e.g., 5-chlorobenzoxazole), alkoxy-carbonyl-benzoxazoles (e.g., 5-ethoxycarbonyl benzoxazole)], oxazoline nuclei [e.g., alkyloxazolines (e.g., 5,5-dimethyl oxazoline, 5-methyl oxazoline)], pyrrolidine nuclei, piperazine nuclei, imidazole nuclei [e.g., halogenoimidazoles (e.g., 5,6-dichloroimidazole), trifluoromethylimidazoles (e.g., 6-trifluoromethyl-5-chloroimidazole), alkoxy-carbonylimidazoles (e.g., 5-methoxycarbonyl imidazole), and tetrazole nuclei.

$Z^4$  represents the atoms needed to form a ketomethylene-heterocyclic nucleus for example, 2-thiohydantoin nuclei, rhodanine nuclei and 4-oxo-2-thioxo-1,3-oxazolidine nuclei.

$R^3$  is an optionally substituted alkyl or aryl group, as was defined for  $R^1$  and  $R^2$  in general formula (I).

$L^4$  and  $L^5$  each represents an optionally substituted methine group as claimed for  $L^1$ ,  $L^2$  or  $L^3$ .  $m$  is an integer of 0 or 1.

General formula III

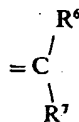


In the above general formula (III):

$Z^3$  represents the atoms needed to form a benzene ring or naphthalene ring. The imidazole nucleus formed therewith may be, for example, halogenobenzimidazole (e.g., 5,6-dichlorobenzimidazole), cyanobenzimidazole (e.g., 5-cyano-benzimidazole), alkoxy-carbonyl benzimidazole (e.g., 5-methoxycarbonyl benzimidazole), naphtho imidazole or hydroxybenzimidazole (e.g., 5-hydroxy-benzimidazole).

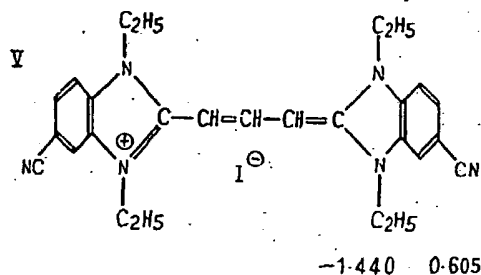
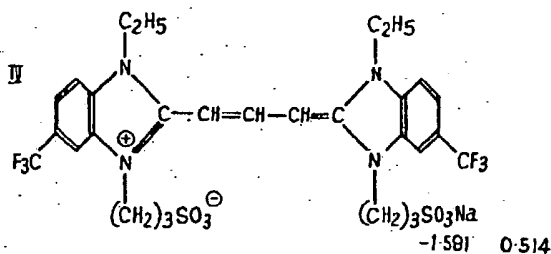
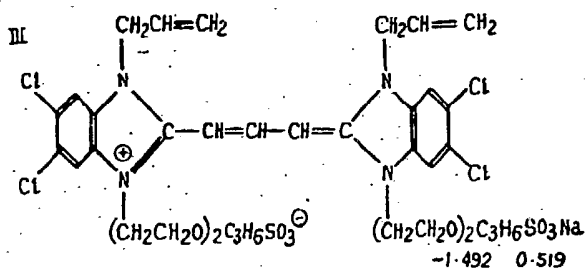
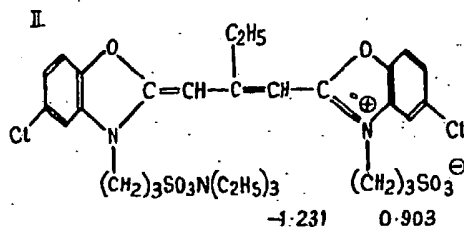
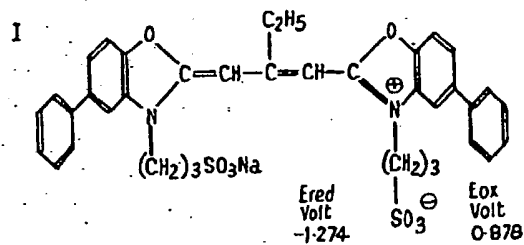
$R^4$  and  $R^5$  are each optionally substituted alkyl groups or aryl groups, as was defined for  $R^1$  and  $R^2$  in general formula (I).

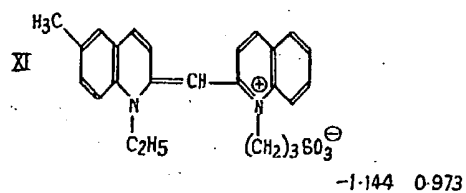
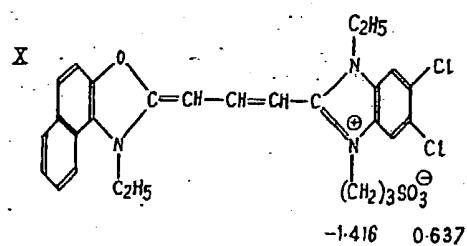
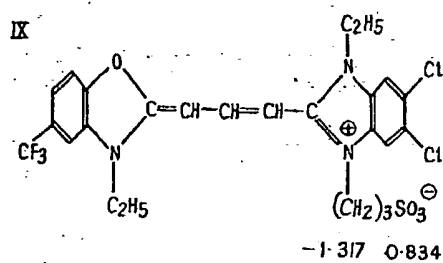
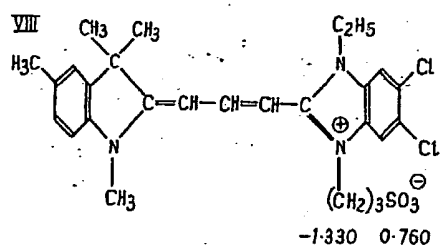
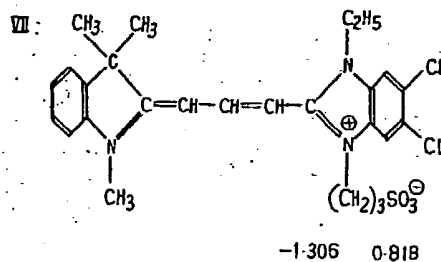
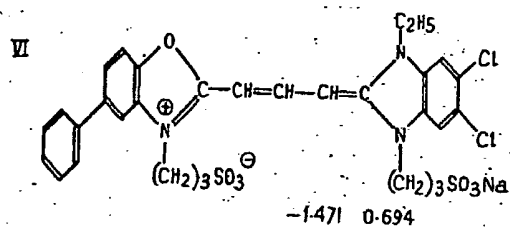
$W$  represents a divalent group and typically includes, for example  $=N-A$  wherein  $A$  is an aryl group wherein the aryl moiety contains a benzene ring,

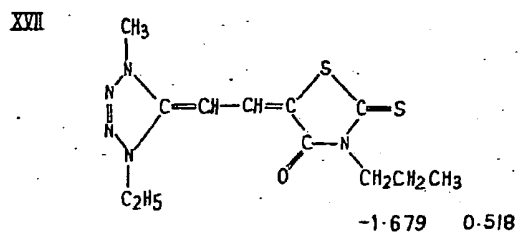
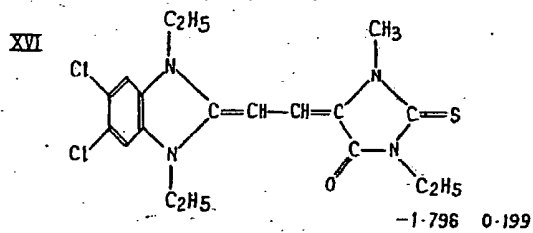
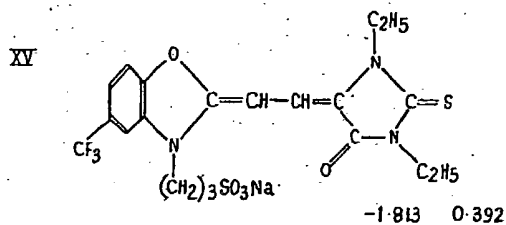
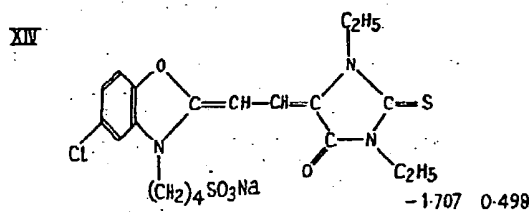
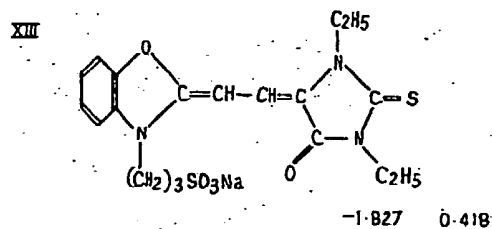
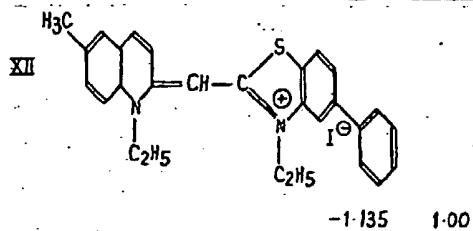


group wherein the alkyl moiety preferably has 1—4 carbon atoms (e.g., methoxy carbonyl or ethoxy carbonyl), five and/or six membered nitrogen-containing heterocyclic nuclei usually contained in cyanine dyes (e.g., benzimidazole or benzothiazole), an aryl group wherein the aryl moiety contains a benzene ring (e.g., phenyl or aminophenyl) or a cyano group.  $n$  is 0, 1 or 2.

Examples of 27 specific dyes employed as sensitizers in this invention are shown hereinbelow together with their respective Ered and Eox values.

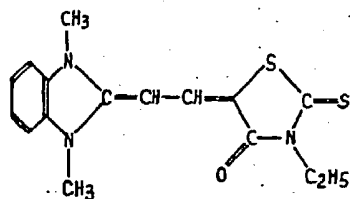






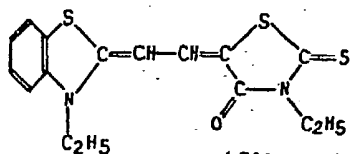


XVIII



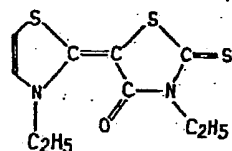
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XIX



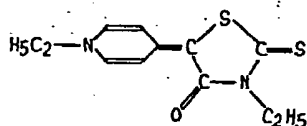
-1.532 0.633

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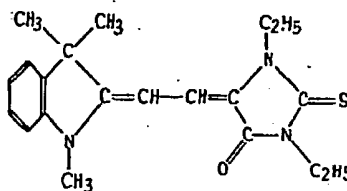
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XXI



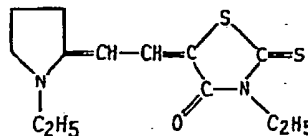
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XXII



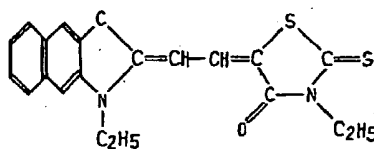
-1.707 0.498

XXIII



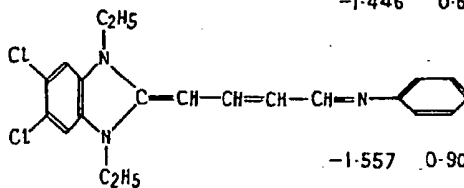
-1.570 0.556

XXIV

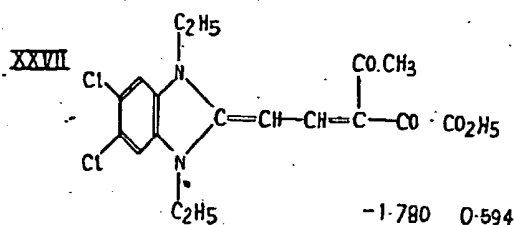
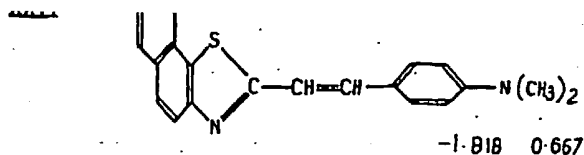


-1.446 0.672

XXV



-1.557 0.903



The sensitizing dye used in this invention is preferably present in an amount of  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  mole per mole of the silver halide.

The effect of the values of Ered and Eox will be demonstrated with reference to the following Table 1, in which dye (I) is a sensitizer according to the invention, dyes (a), (c) and (e) lie outside the scope of the invention since their values of Eox are greater than 1.00, while dyes (d) and (b) are outside the scope of the invention since the difference between their values of Eox and Ered is below 2.00.

TABLE 1

Dye	Ered (volt)	Eox (volt)
Dye (I) Anhydro-5,5'-diphenyl-3,3'-disulphopropylbenzoxa-9-ethyl trimethine hydroxide	-1.274	0.878
Dye (a) 3,3'-diethyl benzoxa-mono methine bromide	-1.700	1.494
Dye (b) 3,3'-diethylbenzoxa-pentamethine iodide	-1.010	0.647
Dye (c) Anhydro(6-methyl-1-ethyl-2-quinoline)-5-ethoxycarbonyl-3-sulphobutyl monomethine hydroxide	-1.215	1.131
Dye (d) Anhydro-3-(sulphopropyl)-4,5,4'-5'-dibenzothia-9-ethyl-3'-sulphopropyl trimethine cyanine hydroxide	-1.211	0.591
Dye (e) Phenosafranine	-0.658	1.460

Comparative dyes (a), (b), (c) and (d) each give low spectral sensitivity, and dye (e) does not give any spectral sensitivity at all. On the other hand, dye (I) gives extremely high spectral sensitivity.

There has hitherto been no clear understanding of the mechanism of spectral sensitization of silver halide particles containing more than 30 mole % of silver iodide. We have found that the dyes included in zone I of Fig. 1 give highly increased sensitivity independently of whether they are used alone or in combination with a supersensitizer.

The second characteristic feature of this invention resides in the nature of the silver halide composition, such as silver bromoiodide, silver chlorobromoiodide or silver iodide; it comprises at least 30 mole %, preferably at least 40 mole %, of silver iodide particles.

The silver iodide particles may have incorporated therewith a minor quantity

of other metallic compounds, such as salts of Group Ib metals of the Periodic Table (e.g., a gold salt or copper salt), salts of Group IIb metals (e.g., a mercury or cadmium salt), salts of Group III metals (e.g., a thallium salt), salts of Group V metals (e.g., a tin or lead salt) and salts of Group VIII metals (e.g., a palladium, iridium or platinum salt). It is preferred to use these metal compound(s) in an amount of from  $10^{-7}$  to  $10^{-3}$  mole based on 1 mole of Ag of the silver halide.

Such metal salts may be with, for example, a mineral acid (e.g., metal chloride or metal sulphate) or a complex salt with, for example, an alkali metal ion, an alkaline earth metal ion, or an ammonium ion (e.g., octahedral metal complex groups as anions), such as zinc chloride, cadmium chloride, gold chloride, mercuric sulphate, thallium sulphate, sodium hexahalogeno ruthenate, sodium hexahalogeno palladate, sodium hexahalogeno iridate and sodium hexahalogeno platinate.

The grain size of the silver halide(s) used in this invention is not particularly limited, but a particularly preferred grain size is within the range of from  $0.005 \mu$  to  $0.8 \mu$  in diameter (measured by the "projected area" method). The silver halides used can however be either coarse grains or fine grains.

Due to the relatively small solubility of silver iodide particles, the rate of crystal growth is so slow that they tend to cause cohesion or agglomeration of the particles, and it is necessary to employ special methods for preparing the silver iodide emulsion. Examples of such methods are as follows:

(a) A solvent for silver iodide, such as ammonia, and an excess of potassium iodide solution are used.

(b) A gelatin-based photographic emulsion containing silver bromide or silver chloride particles, or mixed silver halide particles thereof, can be subjected to conversion by reacting with iodine ions.

(c) A suitable organic silver salt (such as silver behenate, silver stearate, silver palmitate, silver myristate, silver laurate, silver benzotriazole, silver salicylate or silver phthalazinone) is firstly dispersed, if desired, in a binder (e.g., polyvinyl butyral and polyvinyl pyrrolidone), and then an iodide compound such as ammonium iodide, mercury iodide or cadmium iodide is added thereto to prepare a silver iodide photosensitive emulsion. This third method is extremely useful for preparing heat-developable photosensitive material (as described below), which can be formed by simply adding to the resultant emulsion a suitable reducing agent.

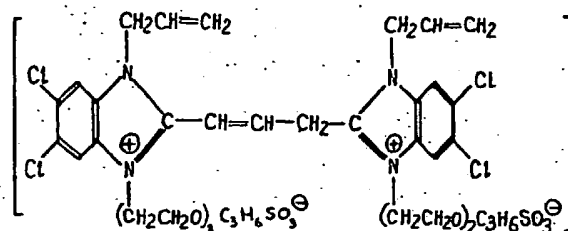
Fourthly, silver or silver salt deposited on the surface of a suitable support is contacted with iodine gas so as to form silver iodide particles on the support. The support can then be coated with a layer of a suitable binder (see below) to form a photosensitive material.

The photosensitive silver halide elements of the invention may be prepared as follows.

The sensitizing dye may be added to the photosensitive silver halide emulsion as a solution in a water-soluble organic solvent such as methanol, ethanol, butanol, ketones, pyridine or an alkoxy ethanol.

The sensitizing dye may be directly added in finely divided form to the emulsion and dissolved in the colloidal binder of the emulsion (by which it is adsorbed onto the silver halide). Alternatively, the sensitizing organic compound may be added to the emulsion after being dissolved in water or an organic solvent together with a proton donor silver ions or other metallic ions. Examples of the best organic solvents used are methanol, ethanol, pyridine, butanol, dimethyl sulphoxide or 2-methoxy ethanol. The most preferred proton donors are mineral or organic acids such as hydrochloric acid, sulphuric acid, methyl sulphonate, benzene sulphonate or perchloric acid. Examples of the other metallic ions are noble metal ions such as gold ions and mercury ions.

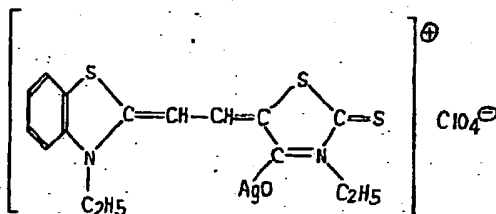
In the case when the proton source or silver ion is present in a sufficient amount together with the dye, a complex salt or adduct is formed therebetween. For instance, when 0.5 ml. of 0.1 N hydrogen chloride solution is added to 100 ml. of a  $1 \times 10^{-3}$  mole methanol solution of dye III, there is formed a complex salt having the following formula:



When this complex salt is added to a silver halid photographic emulsion, it is neutralized under ordinary pH conditions (i.e., pH = 6.0 — 7.5) with the dissociation of the proton.

Accordingly, there results the same condition of adsorption (of the dye to silver halide) as if a methanol solution of the dye III was added thereto.

In another example, 1 ml. of a 0.1 N solution of silver perchlorate ( $\text{AgClO}_4$ ) is added to 100 ml. of a  $1 \times 10^{-3}$  mole methanol solution of dye XIX, and there is formed in the resultant solution a complex ion having the following formula:



When this ion is added to a silver halide photographic emulsion, dissociation of silver ion takes place under normal conditions (i.e.,  $\text{pAg} = 5.0 - 10$ ). Accordingly, the same adsorption of the dye on the silver halide results as if silver ions had been prepared in the emulsion in an amount equivalent to that brought into the emulsion.

The sensitizing dye may also be added to the silver halide emulsion after it has been dissolved in an oil solvent and the resultant oily solution dispersed into the emulsion as minute oily globules, the size of which can be as small as 1 micron or less.

Any other technique which has been commonly employed for the addition of such a material to a gelatin-based silver halide photographic emulsion may be employed.

Various protective colloids which have been known and widely used in conventional photosensitive silver halide materials may be used as binder in this invention. Examples of such protective colloids used in the photosensitive silver halide element of this invention include gelatin and gelatin derivatives (e.g., those described in our copending Patent Application Serial No. 1,396,970 i.e., the reaction products of gelatin with aromatic or aliphatic acid anhydrides, halogen atom-containing compounds, isocyanates, N-acryl vinyl sulphonamide, for example, phthalated gelatin, acetylated gelatin, gelatin maleate, carboxymethyl gelatin, gelatin benzene sulphonate, gelatin trimellitate, gelatin benzoate, gelatin sulfo-phthalate or gelatin succinate), and water soluble synthetic polymers such as polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl methyl methacrylate and copolymers thereof.

Where the silver halide which has been prepared by converting a suitable organic silver salt with a halide salt containing iodine ions the binder is preferably a polymer such as polyvinyl butyral, polyvinyl methyl methacrylate, cellulose acetate butyrate, polyvinyl chloride, polyisobutylene or polyethylene oxide.

Furthermore, they may be used in combination with polymer latices and matting agents.

The emulsion usually contains 0.0001 to 3.0 moles of silver halide per 100 grams of binder. The silver halide emulsion in this invention may also contain any of a variety of known additives, such as materials capable of improving photosensitivity, i.e., chemical sensitizers, stabilizers, fog-inhibitors; materials capable of accelerating developing speed, e.g., reducing agents acting as developing agents, developing aids, e.g., polyalkylene oxide and organic amine compounds, coating aids and hardeners; and dyes and pigments.

The emulsion is then coated on a support; typical support materials generally employed in this invention include, for example, cellulose acetate, cellulose nitrate, polyvinyl acetal, polystyrene, polyethylene terephthalate, polycarbonates, paper (including baryta paper and resin-laminated papers), synthetic paper and metal sheets; dyes or pigments may be included in the support.

A preferred embodiment of the invention will now be described at length, namely the heat-developable element mentioned previously. These elements comprise, coated on a support, (1) an organic silver salt, (2) a light-sensitive silver halide, (3) a reducing agent and (4) a sensitizing dye as hereinbefore disclosed.

The organic silver salts used in the heat-developable element are not particularly limited so long as, of course, they function in the heat-developable light-sensitive material of the present invention to provide an image of sufficient density. Most preferred are, however, silver salts of organic carboxylic acids and silver salts of heterocyclic compounds containing an imino group or mercapto group. The most preferred silver salts of organic carboxylic acids are those of aliphatic carboxylic acids having more than 10 carbon atoms in the chain.

Specific examples of such organic silver salts used in this embodiment are silver salts of aliphatic carboxylic acids such as silver laurate, silver myristate, silver palmitate, silver stearate and silver behenate, silver caprate, as well as the silver salt of benzotriazole, the silver salt of saccharin, the silver salt of phthalazinone, silver phthalate, silver terephthalate and silver salicylate. These organic silver salts are relatively stable to light and, when exposed to light, are reduced by a reducing agent upon heating by the catalytic action of a silver halide, to give a silver image. Preferred organic silver salts as may be used in the present invention have sausage-shaped particles where the overall length is 0.01—5 microns, preferably 0.1—1 micron, and the thickness or diameter (measured normal to the overall length) is 0.0001—0.5 microns, preferably 0.005—0.1 microns. The organic silver salts may however, be substantially spherical, preferably having a diameter of 0.01 to 5 microns, more preferably 0.1 to 1 micron.

The amount of the organic silver salt used in this embodiment is that necessary to provide an image of sufficient density. The visual acuity of users will vary greatly, but in general from 0.2 to 3 g/m<sup>2</sup>, calculated as silver, should be applied to the support. Preferably, to provide a safety factor, at least 0.4 g/m<sup>2</sup> is used, but seldom will more than 2 g/m<sup>2</sup> be used. Above 3 g/m<sup>2</sup>, costs are increased without any substantial benefit in image density.

As the reducing agent of this embodiment, any compound capable of reducing the organic silver salt to give a silver image when heated in the presence of exposed silver halide can be used, for example, substituted phenols, substituted or unsubstituted bisphenols, substituted or unsubstituted bisnaphthols or naphthols, di- or higher poly-hydroxybenzenes such as hydroquinone derivatives, ascorbic acid and its derivatives, di- or higher poly-naphthalenes and 3-pyrazolidones, for instance, including hydroquinone mono ethers, ascorbic acid or mono- or di-carboxylic acid esters of ascorbic acid, reducing sugar, 5-hydroxy-2-hydroxymethyl- $\gamma$ -pyrone, 4-isopropyltropolones, substituted or unsubstituted 1-aryl-3-pyrazolidones, which can be alkyl (C<sub>1</sub>—C<sub>8</sub>), alkoxy (C<sub>1</sub>—C<sub>8</sub>), phenyl, halogen, amino, alkyl-substituted amino (C<sub>1</sub>—C<sub>8</sub>), which may be acetyl or nitro substituted.

Specific examples of such materials are: hydroquinone, methylhydroquinone, chlorohydroquinone, bromohydroquinone, phenylhydroquinone, hydroquinone mono-sulphonate, *t*-octylhydroquinone, *t*-butylhydroquinone, 2,5-dimethylhydroquinone, 2,6-dimethylhydroquinone, methoxyhydroquinone, ethoxyhydroquinone, *p*-methoxyphenol, *p*-ethoxyphenol, hydroquinone monobenzyloether, catechol, pyrogallol, resorcinol, *p*-aminophenol, *o*-aminophenol, *N*-methyl-*p*-aminophenol, 2-methoxy-4-aminophenol, 2,4-di-aminophenol, 2- $\beta$ -hydroxyethyl-4-aminophenol, *p*-*t*-butylphenol, *p*-*t*-amylphenol, *p*-cresol, 2,6-di-*t*-butyl-*p*-cresol, *p*-acetophenol, *p*-phenylphenol, *o*-phenylphenol, 1,4-dimethoxyphenol, 3,4-xyleneol, 2,4-xylenol, 2,6-dimethoxyphenol, 1-amino-2-naphthol-6-sulphonic acid sodium salt, 1-naphthylamine-7-sulphonic acid, 1-hydroxy-4-methoxy-naphthalene, 1-hydroxy-4-ethoxy-naphthalene, 1,4-dihydroxynaphthalene, 1,3-dihydroxy-naphthalene, 1-hydroxy-4-aminonaphthalene, 1,5-dihydroxynaphthalene, 1-hydroxy-2-phenyl-4-methoxynaphthalene, 1-hydroxy-2-methyl-4-methoxynaphthalene,  $\alpha$ -naphthol,  $\beta$ -naphthol, 1,1'-dihydroxy-2,2'-binaphthyl, 4,4'-dimethoxy-1,1'-dihydroxy-2,2'-binaphthyl, 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl, 6,6'-dinitro-2,2'-dihydroxy-1,1'-binaphthyl, bis(2-hydroxy-1-naphthyl)methane, bisphenol A, 1,1-bis-(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane, 2,4,4-trimethylpentyl-bis-(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane, 2,4,4-trimethylpentyl-bis-(2-

hydroxy-3,5-dimethylphenyl)methane, bis - (2-hydroxy-3-*t*-butyl-5-methylphenyl)-methane, bis-(2-hydroxy-3,5-di-*t*-butylphenyl)methane, 4,4'-methylene-bis-(3-methyl-5-*t*-butylphenol), 4,4'-methylenebis-(2,6-di-*t*-butylphenol), 2,2'-methylene-bis - (2-*t*-butyl-4-ethylphenol), 2,6-methylenebis-(2-hydroxy-3-*t*-butyl-2-methylphenyl)-4-methylphenol, 3,3',5,5'-tetra-*t*-butyl-4,4'-dihydroxy-biphenyl, 1-ascorbic acid, 1-ascorbic acid monoester, 1-ascorbic acid diester, *p*-oxyphenylglycine, N,N-diethyl-*p*-phenylene diamine, furoin, benzoin, dihydroxyacetone, glycerine-aldehyde, rhodizonic acid, tetrahydroxyquinone, methyl gallate, propyl gallate, hydroxytetrone acid, N,N-di-(2-ethoxyethyl)hydroxylamine, glucose, lactose, 1-phenyl-3-pyrazolidone, 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone, bis-(3-methyl-4-hydroxy-5-*t*-butylphenyl)-sulphide, 3,5-di-*t*-butyl-4-pyrazolidone, bis-methylamine and  $\alpha,\alpha'$ -(3,5-di-*t*-butyl-4-hydroxyphenyl)-dimethylether.

A relatively strong reducing agent such as a bisphenol is suitable for a silver salt of a higher fatty acid such as silver behenate, while a relatively weak reducing agent such as a substituted phenol is suitable for a silver salt of a lower fatty acid such as silver laurate. When a weak reducing agent such as *p*-(*t*-butyl)-phenol is used for silver behenate, for example, only a low density image is obtained, and when a strong reducing agent such as hydroquinone is used for silver laurate, for example, the fog increases with a lowering of the contrast of the image.

The quantity of the reducing agent to be used in these embodiments will depend on the specific organic silver salt and reducing agent combination, but is preferably 0.1 to 5 moles per mole of the organic silver salt, more preferably 0.5 mole to 1 mole per mole of the organic silver salt.

In heat-developable photosensitive materials, the light-sensitive silver halide (at least 30 mole % being silver iodide) in a catalytic amount can be previously prepared and added as one constituent of the light-sensitive layer of the invention and may be added as a photographic silver halide emulsion, but it is preferred to form the silver halide *in situ* by reacting the organic silver salt as a constituent of the light-sensitive layer of the invention with a halide capable of forming the light-sensitive silver halide. For example, a halide such as ammonium iodide is added to a polymeric dispersion of silver laurate prepared as mentioned hereinbefore, whereby a part of the silver laurate and ammonium iodide are reacted to form silver iodide, which is confirmed by a change in the X-ray diffraction pattern of the system.

Halides suitable for thus forming the silver halide include inorganic halogen compounds represented, for example, by  $MX_n$  in which M represents a hydrogen atom, ammonium group or metal atom, X represents halogen at least 30 mole % of which is iodide and *n* represents the atomic valence of M. Illustrative of such halides are iodides of hydrogen, ammonium, strontium, cadmium, zinc, tin, chromium, sodium, barium, iron, cesium, lanthanum, copper, calcium, nickel, magnesium, potassium, aluminium, antimony, gold, cobalt, mercury, lead, beryllium, lithium, manganese, gallium, indium, rhodium, ruthenium, palladium, iridium, platinum, thallium, bismuth and mixtures thereof. Furthermore, organic halides such as methyl iodide, ethyl iodide, octyl iodide and butyl iodide, and halogenated hydrocarbons such as iodoform (triiodomethane), can also be used with success.

The quantity of the light-sensitive silver halide or halide present for forming the same is preferably 0.001 to 0.5 mole per mole of the organic silver salt, more preferably 0.01 mole to 0.1 mole of the halide per mole of the organic silver salt. The reaction of the halide to form silver halide is substantially stoichiometric. If less than about 0.001 mole is used, the sensitivity is lowered, while if more than about 0.5 mole is used, the quantity of silver halide becomes too high. As the silver halide gradually blackens under the influence of room light, excessive silver halide leads to a blackening of the non-image area of a heat-developed material when it is allowed to stand under room light and, consequently, to a decrease of contrast of the image.

The reaction of the inorganic or organic halide with the organic silver salt proceeds easily and substantially stoichiometrically, and it suffices to mix the inorganic or organic halide with a polymer dispersion of the organic silver salt at room temperature for a time of 1 second to 60 minutes, with common reaction times sufficient for the reaction to be completed being 30 seconds to 30 minutes, and typically at 0°C to 80°C, more preferably at 20°C to 60°C, under atmospheric pressure; the use of other pressures is unnecessary.

In the heat-developable light-sensitive composition used in some embodiments of the invention there may be incorporated any binder which is

ordinarily hydrophobic, but hydrophilic binders can also be used. The binders are transparent or semitransparent, for example, natural materials such as gelatin, gelatin derivatives and cellulose derivatives, and synthetic polymeric substances such as polyvinyl compounds and acrylamide polymers. Other synthetic polymer compounds used are dispersed vinyl compounds of the latex type.

Moreover, desirable high molecular weight materials and resins include polyvinyl butyral, cellulose acetate butyrate, polymethyl methacrylate, polyvinyl pyrrolidone, ethyl cellulose, polystyrene, polyvinyl chloride, cellulose propionate, cellulose nitrate, phthalated gelatin, polyvinyl acetate, polyvinylidene chloride, polyvinyl formal chlorinated rubber, polyisobutylene, butadiene-styrene copolymers, vinyl chloride-vinyl acetate copolymers, vinyl acetate-vinyl chloride-maleic acid copolymers and polyvinyl alcohol. The weight ratio of the binder to the organic silver salt is preferably 4 to 1 to 1 to 4 parts.

Any material can be used as the support member of the heat-developable light-sensitive material of the invention; typical supports are cellulose nitrate films, cellulose ester films, poly(vinyl acetal) films, polystyrene films, polyethylene terephthalate films, polycarbonate films, resinous materials, glass, paper and metals. The only limitation on the support member is that it not be excessively degraded during the exposure or heat development steps nor, of course, be composed of a material which would adversely affect the light-sensitive elements.

The thickness of the heat-developable light-sensitive layer can vary greatly in the present invention, but generally speaking, thicknesses of from 1 micron to 15 microns, more preferably 3 microns to 10 microns, are used in combination with an overcoat layer having a thickness of from 1 micron to 20 microns, more preferably 2 microns to 10 microns.

The heat-developable light-sensitive material used for the practice of the invention can be provided with an anti-static layer or an electrically conductive layer. Moreover, an antihalation substance or antihalation dye can be incorporated in the light sensitive layer. It is preferred that the sensitive layer be overcoated with a polymer layer, preferably of a polymer which withstands temperatures above 115°F is colourless and is soluble in an organic solvent used to form the overcoating layer as claimed in our copending application No. 21993/73 (Ser. No. 1,387,541).

The heat-developable light-sensitive material according to the invention may further contain a matting agent such as starch, titanium dioxide, zinc oxide or silica, and a brightening agent of the stilbene type, triazine type, oxazole type or coumarin type.

The heat-developable light-sensitive layer according to the invention can be coated by various coating methods, for example, an immersion method, an air-knife method, a curtain coating method and an extrusion coating method using a hopper as described in U.S. Patent 2,681,294. If desired, two or more layers can simultaneously be coated.

Furthermore, optical sensitizing dyes may be used in the elements of the invention so as to impart light-sensitivity thereto. Optical sensitization is ordinarily carried out, for example, by adding a sensitizing dye in the form of a solution or dispersion in an organic solvent. As such optical sensitizers, hemicyanine, cyanine and merocyanine dyes are usually used.

A latent image formed by exposing the above-mentioned elements of the heat-developable light-sensitive material to a light source such as a xenon lamp, tungsten lamp or mercury lamp can be developed merely by heating the elements. In embodiments of the invention, a latent image in the elements of the exposed heat-developable light-sensitive material may be developed by heating at 100° to 160°C until the desired image is developed. The developing temperature is preferably 110° to 140°C. Within the broad temperature range, a higher temperature or lower temperature may optionally be used by shortening or lengthening the heating time. A developed and stabilized image is ordinarily obtained in 1 to 60 seconds. The heating of the above-mentioned elements can be carried out by any suitable method such as by contacting the elements with a simple heating plate, contacting them with a heating drum, passing them through a heating space or subjecting them to high-frequency heating.

Detailed procedures for preparing typical silver iodide photosensitive elements used in this invention will be given in the following examples:

Preparation Example 1:

(A) Twelve grams of gelatin and 32 g of potassium iodide are weighed and dissolved in 160 ml of water to give Solution 1. 40 g of silver nitrate are dissolved in

80 ml of water to give Solution 2. 39 g of potassium iodide are dissolved in 80 ml of water to give Solution 3. While maintaining Solution 1 at 65°C, solutions 2 and 3 are added with stirring over 20 minutes. After ripening the resultant silver halide dispersion for 30 minutes, an aqueous gelatin solution in which 40 g of inert gelatin is dissolved in 140 ml of water is added thereto and the mixture so obtained is rapidly cooled, to set it, and is then washed with water. Thus a photosensitive emulsion, Emulsion A, is obtained.

(B) The procedure for preparing Emulsion A is repeated except that an aqueous solution containing 33.6 g of potassium bromide and 31.2 g of potassium iodide dissolved in 80 ml of water is used instead of Solution 3. Thus, Emulsion B is obtained.

(C) 20 g of gelatin and 15.7 g of sodium chloride are dissolved in 560 ml of water to give Solution 1. 195 g of silver nitrate are dissolved in 520 ml of water to give Solution 2. 78 g of sodium chloride are dissolved in 320 ml of water to give Solution 3. 200 g of potassium iodide are dissolved in 500 ml of water to give Solution 4. To Solution 1, maintained at 40°C, there are simultaneously added, with stirring, Solutions 2 and 3. After ripening the mixture at 45°C for one minute, Solution 4 is added and the resultant mixture is further ripened for another 20 minutes. To the resultant mixture, 235 g of powdery gelatin is added and the mixture ripened again for 30 minutes. After setting and washing with water, Emulsion C is obtained.

(D) The same procedure is employed as for preparing Emulsion A, except that the period for ripening is shortened to one minute; thus there is obtained Emulsion D.

Preparation Example 2:

To a solution of 10 g of behenic acid in 100 ml of *n*-butyl acetate kept at 10°C, there was dropwise added a solution of 0.5 g of  $\text{Hg}(\text{NO}_3)_2$  in 100 ml of water which had previously been acidified with nitric acid to a pH of 2. The resultant solution was further mixed with 50 ml of a 1 mole % aqueous solution of a silver nitrate-ammonia complex, thereby to prepare silver behenate, which was then rinsed with water and methanol. The rinsed silver behenate was dispersed in 120 g of a 15% by weight solution of polyvinyl butyral in isopropanol. To 20 g of the thus-obtained dispersion was added 1 ml of a 32% solution of ammonium iodide in methanol to prepare a photosensitive emulsion.

The invention will be more fully explained by the following Examples.

EXAMPLE 1.

Samples each of one kilogram of gelatin-silver iodide Emulsion A were prepared as in Preparation Example 1(A) and had an iodine content of 100 mole %, an average particle diameter of 1 micron, a pAg of 5.4 and a silver iodide/binder ratio of 0.45 mole/100 g. Emulsion A samples were added to methanol solutions each containing a given amount of a dye as shown in Table 1. To each of the resultant solutions was further added 20 ml of a 2 weight % solution of a hardener (sodium salt of 1,4-dichloro-6-hydroxytriazine) and a coating aid (20 ml of a 1 weight % solution of sodium nonylbenzene sulphonate). The solution so obtained was then applied to a cellulose triacetate film to a dry coating thickness of 5.0  $\mu$ . After drying, a sample film of the photosensitive material was obtained.

The sample was cut into strips and subjected to a sensitometry test by being exposed through an optical wedge to a tungsten light source having a colour temperature of 2854°K through a No. K-12 yellow filter or a BPB blue filter sold by Fuji Photo Film Co.; The exposure details were 1000 lux for 10 sec.)

The exposed film was developed at 20°C for 10 minutes, fixed, washed with water and dried, the developer having the following composition:

Water	500 ml
Metol	2 g
Anhydrous sodium sulphite	90 g
Hydroquinone	8 g
Sodium carbonate monohydrate	52.5 g
Potassium bromide	5 g
Water to make	1000 ml

The strips were subjected to densitometry using an S-type densitometer manufactured by Fuji Photo Film Co. to determine their densities, from which characteristic curves were obtained.

The results are given in Table 2.

Meanwhile, identical strips were exposed with a spectrographic camera and developed in a similar manner to obtain a spectrogram.

It will be seen from Table 2 that the organic dye(s) used in this invention have a particularly strong sensitizing effect.



TABLE 2

Test No.	Organic compound used		Relative yellow filter ** sensitivity	Relative blue filter *** sensitivity	Fogging	Spectrogram
	Dye	Molar concentration per liter ml.				
1 (control)	None	—	*	100	0.04	Fig. 2, Curve 1
2	1	( $2 \times 10^{-3}$ ) 20	100	100	0.04	Fig. 2, Curve 2
		40	107	126	0.06	
		80	118	76	0.07	
3 (comparison)	(a)	( $4 \times 10^{-3}$ ) 10		107	0.04	Fig. 3, ,, 3
		20		107	0.04	
4 (comparison)	(b)	( $1 \times 10^{-3}$ ) 40	18	79	0.06	Fig. 3, ,, 4
			12	43	0.08	
5 (comparison)	(c)	( $4 \times 10^{-3}$ ) 10		85	0.04	Fig. 4
		20		70	0.04	
6 (comparison)	(d)	( $5 \times 10^{-3}$ ) 40	18	67	0.05	Fig. 5 ,, 6
		80	18	63	0.06	
7 (comparison)	(e)	( $1 \times 10^{-3}$ ) 20		66	0.04	Fig. 6, ,, 7
		80		60	0.05	

\* The sensitivity was so low that the value could not be calculated.

\*\* The relative yellow filter sensitivity is given as a relative sensitivity by taking the sensitivity of dye I (20 ml.,  $2 \times 10^{-3}$  molar concentration per liter) as 100.

\*\*\* The relative blue filter sensitivity is given as a relative sensitivity by taking the sensitivity where no dye is present in the element as 100.

The procedure of Example 1 was repeated except that 1 kg of gelatin-silver iodobromide Emulsion B (iodine content: 97 mole %; average particle diameter measured by projected area: 0.6  $\mu$ ; pAg: 5.4; silver halide/binder ratio: 0.45 mole/100 g) was used as the photosensitive emulsion. The results are given in Table 3 with the dyes and amounts used.

### EXAMPLE 3.

The procedure of Example 1 was repeated except that 1 kg of gelatin-silver iodobromide Emulsion C (iodine content: 95 mole %; average particle size: 0.2  $\mu$ ; pAg: 7.31; silver halide/binder ratio: 0.45 mole/100 g) was used as the photosensitive emulsion. The results are given in Table 4 with the dyes and amounts used.

### EXAMPLE 4.

To a solution of 6 g of benzotriazole in 100 ml of tricresyl phosphate kept at 15°C there was dropwise added 100 ml of 1 mole % aqueous solution at 0°C of an  $\text{AgNO}_3$ -ammonia complex. The complex salt was a silver amine complex which could be written as  $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ . The thus-obtained silver benzotriazole was washed with water and acetone, then dispersed in 120 g of a 15% by weight solution of polyvinyl butyral in isopropanol, using a ball mill. The thus-obtained silver benzotriazole had a spindle-like or sausage shape with an overall length (along the major axis) of approximately 3  $\mu$  and a minor axis length of approximately 0.04  $\mu$ .

A liquid coating composition was prepared by adding to 40 g of the above silver salt dispersion the following components at room temperature over 20 minutes:

	Sample A	Sample B
Ascorbic acid monopalmitate	2 g	2 g
2-Methoxy ethanol	8 ml	8 ml
$\text{NH}_4\text{I}$ (8.5% by weight solution in methanol)	1 ml	1 ml
Dye XIII (0.2% by weight solution in methanol)	nil	2 ml
2-Mercapto-3,4-methylthiazole (2% by weight solution in 2-methoxy ethanol)	1 ml	1 ml

The above coating composition was applied to a polyethylene terephthalate support in such an amount that the coated film carried 1.2 g of silver per square metre. It was then dried at 50°C for 30 minutes.

The thus coated, dried film was further top-coated with a 15% tetrahydrofuran solution of an 85:15 by weight vinyl chloride-vinyl acetate copolymer, then dried at 50°C for an hour. The thus obtained heat-developable photosensitive material was exposed with a tungsten lamp at an exposure of 250,000 lux through a toned negative pattern, and then thermally developed by heating at 130°C for 30 seconds. As a result of this exposure test, Sample A gave only a dim positive image, while Sample B gave a high-contrast, deeply toned clear positive image.

The spectrogram obtained from Sample A is given as Curve 19 of Fig. 18 and that of Sample B as Curve 20 of Fig. 18. As is seen from the spectrogram, Sample A had a peak at about 425 nm, but Sample B gave a spectrally sensitized peak at about 520 nm in addition to a peak at about 425 nm.

### EXAMPLE 5.

To a solution of 11 g of lauric acid in 100 ml of *n*-butyl acetate kept at 10°C there was dropwise added 100 ml of an aqueous solution of 20.5 g of  $\text{Hg}(\text{NO}_3)_2$  which had been acidified to a pH of 2 with nitric acid. The resultant solution was further combined with 50 ml of a 1 mole % solution of an ammoniacal complex of  $\text{AgNO}_3$  as in Example 4 to prepare silver laurate. The silver laurate was washed

with water and methanol and then dispersed in 120 g of 15% by weight solution of polyvinyl butyral in isopropanol. The silver laurate was in the form of globules of an approximate diameter of 0.1  $\mu$ .

A liquid coating composition was prepared by adding 20 g of the silver laurate dispersion to the following composition at room temperature over 20 minutes:

	Sample A	Sample B
NH <sub>4</sub> I (3.2% by weight solution in methanol)	1 ml	1 ml
Dye I (0.1% by weight solution in methanol)	nil	1 ml
Phthalazinone (25% by weight solution in 2-methoxy-ethanol)	1 ml	1 ml
p-Phenyl phenol (70% by weight solution in 2-methoxy-ethanol)	2 ml	2 ml

A polyethylene terephthalate film was coated with the above coating composition so that the coated film carried 1.0 g of silver per square metre, and was then dried at 50°C for 30 minutes. The coated and dried film was further top-coated with a 15% solution in tetrahydrofuran of an 85:15 by weight vinyl chloride-vinyl acetate copolymer and was further dried at 50°C for one hour.

The thus-obtained heat-developable photosensitive material was exposed through a toned negative patterned to a tungsten lamp, at an exposure dosage of 250,000 lux, then thermally developed by heating at 120°C for 20 seconds. Sample A gave only a blurred positive image, whereas Sample B gave a high contrast, deeply toned, clear positive image.

The spectrogram obtained from Sample A is given as Curve 21 in Fig. 19, and that of sample B is given as curve 22 in Fig. 19. According to the spectrograms, Sample A had a peak at about 425 nm, but Sample B showed a spectrally sensitized peak at about 545 nm in addition to the one at about 425 nm.

#### EXAMPLE 6.

To a solution of 5.7 g of behenic acid in 100 ml of *n*-butyl acetate kept at 60°C there was dropwise added 100 ml of an aqueous solution of 0.17 g of Hg(NO<sub>3</sub>)<sub>2</sub>, which had been adjusted to a pH of 2 with nitric acid. The resultant solution was further combined with 50 ml of 1 mole % aqueous solution of an ammoniacal complex salt of AgNO<sub>3</sub> (as in Example 4) to prepare silver behenate. After the silver behenate was washed with water, toluene and acetone, it was dispersed in 40 g of a 15 weight % solution of polyvinyl butyral in isopropanol, using a ball mill. The silver behenate had the form of globules of an approximate diameter of 0.3  $\mu$ .

A liquid coating composition was prepared by adding the following composition to 20 g of the silver behenate dispersion at room temperature over 20 minutes.

	Sample A	Sample B
NH <sub>4</sub> I (3.2% by weight solution in methanol)	1 ml	1 ml
Dye XIX (0.2% by weight solution in chloroform)	nil	1 ml
Phthalazinone (2.2% by weight solution in 2-methoxy-ethanol)	1 ml	1 ml
1,1-Bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethyl hexane (10% by weight solution in acetone)	10 ml	10 ml

According to the procedure of Example 5, Samples A and B were exposed, heated and developed to give positive images.

The spectrogram obtained from Sample A is given as Curve 23 of Fig. 20, and that of Sample B is given as Curve 24 of Fig. 20. It will be noted that Sample A gives a peak at about 425 nm, while sample B has peaks at both about 575 nm and about 425 nm.

TABLE 3

Test No.	Organic compound used			Relative yellow filter sensitivity	Relative blue filter sensitivity	Fog
	Dye	Molar concentration per liter	ml.			
8	None	—		*	100	0.1
9	I	$2 \times 10^{-3}$	10	85	100	0.1
			20	100	89	0.1
10	(b) (Comparison)	$2 \times 10^{-3}$	10	63	90	0.1
			20	76	75	0.1
11	(d) (Comparison)	$5 \times 10^{-4}$	20	95	90	0.1
			40	100	85	0.1
12	(e) (Comparison)	$1 \times 10^{-3}$	20	*	50	0.1
			80	*	22	0.1

\* The sensitivity was so low that the value could not be calculated.

TABLE 3 (continued)

Test No.	Organic compound used			Relative yellow filter ** sensitivity	Relative blue filter *** sensitivity	Fogging	Spectrogram
	Dye	Molar concentration per liter	ml.				
13 (control)	None	—		*	100	0.04	
14	II	$(2 \times 10^{-3})$	20	63	85	0.04	Fig. 9, Curve 10
			40	50	71	0.04	
15	III	$(5 \times 10^{-4})$	20	89	112	0.04	Fig. 10, " 11
			40	100	107	0.05	
16	V	$(5 \times 10^{-4})$	40	117	71	0.04	Fig. 11, " 12
			80	91	71	0.04	
17	VI	$(1 \times 10^{-3})$	20	100	79	0.04	Fig. 12, " 13
			40	135	71	0.04	
18	VIII	$(5 \times 10^{-4})$	20	100	92	0.04	Fig. 13, " 14
			40	112	85	0.04	
19	XI + XXVI	$(2 \times 10^{-3})$	40	90	91	0.04	Fig. 14, Curve 15
		$(1 \times 10^{-3})$	10				
	XI + XXVI	$(2 \times 10^{-3})$	40	100	91	0.04	
		$(1 \times 10^{-4})$	20				

TABLE 3 (continued)

Test No.	Organic compound used			Relative yellow filter ** sensitivity	Relative blue filter *** sensitivity	Fogging	Spectrogram
	Dye	Molar concentration per liter	ml.				
20	II + III	(2 × 10 <sup>-3</sup> )	40	86	63	0.04	Fig. 15, Curve 16
		(5 × 10 <sup>-4</sup> )	20				
	II + III	(2 × 10 <sup>-3</sup> )	40	100	60	0.04	
		(5 × 10 <sup>-4</sup> )	40				
21	XXV	(1 × 10 <sup>-3</sup> )	40	50	76	0.04	Fig. 16, „ 17
			80	65	66	0.05	

\* and \*\*\* each has the same meaning as in Table 1.

\*\* The relative yellow filter sensitivity is given as a relative sensitivity taking the sensitivity of Dye III (49 ml., molar concentration of 5 × 10<sup>-3</sup> moles per liter) as 100.

TABLE 4

Test No.	Organic compound used		Relative yellow filter sensitivity <sup>***</sup>	Relative blue filter sensitivity <sup>***</sup>	Fogging	Spectrogram
	Dye	Molar concentration per liter				
22 (contrast)	None	—	— <sup>*</sup>	100	0.04	
23	I	(1 × 10 <sup>-3</sup> )	86	100	0.04	
		80	100	200	0.04	
24	XVI	(1 × 10 <sup>-3</sup> )	112	152	0.04	Fig. 17, Curve 18
		80	158	200	0.05	
		160	200	250	0.05	
		240	200	178	0.06	

<sup>\*</sup> and <sup>\*\*\*</sup> each has the same meaning as in Table 1.

<sup>\*\*</sup>: The relative yellow filter sensitivity is given as a relative sensitivity taking the sensitivity of an emulsion containing Dye I (80 ml., 1 × 10<sup>-3</sup> mole per liter concentration) as 100.

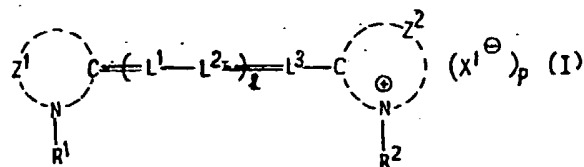
#### WHAT WE CLAIM IS:—

1. A photosensitive composition, which comprises grains of photosensitive silver halide of which at least 30 mole % is silver iodide, and a spectrally sensitizing dye adsorbed on the surface of the silver halide grains, which sensitizing dye has an oxidation potential not exceeding 1.00 volt and a difference in values between its oxidation potential and its reduction potential of at least 2.00 volts.

2. A photosensitive composition as claimed in Claim 1, wherein the sensitizing dye is a merocyanine or hemicyanine dye.

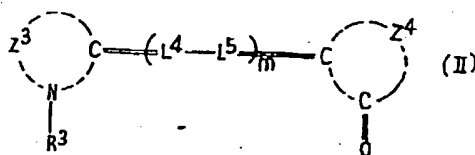
3. A photosensitive composition as claimed in Claim 2, wherein the dye has no methine bridge or has a polymethine bridge.

4. A photosensitive composition as claimed in Claim 1, 2 or 3, wherein the sensitizing dye has the general formula I:



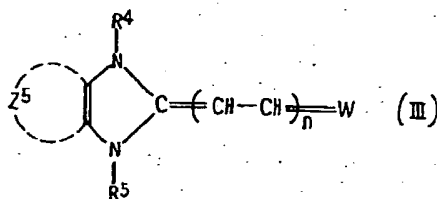
wherein  $\text{Z}^1$  and  $\text{Z}^2$  each represents the atoms needed to form a five- or six-membered nitrogen-containing heterocyclic nucleus,  $\text{L}^1$ ,  $\text{L}^2$  and  $\text{L}^3$  each represents an optionally substituted methine group,  $\text{R}^1$  and  $\text{R}^2$  each represents an optionally substituted alkyl or aryl group,  $\text{X}^1$  represents an anion,  $l$  is 0 or 1, and  $p$  is 0 or 1.

5. A photosensitive composition as claimed in Claim 1, 2 or 3, wherein the sensitizing dye has the general formula:



wherein  $\text{Z}^3$  represents the atoms needed to form a five- or six-membered nitrogen-containing heterocyclic nucleus,  $\text{Z}^4$  represents the atoms needed to form a ketomethylene-heterocyclic nucleus,  $\text{R}^3$  is an optionally substituted alkyl or aryl group,  $\text{L}^4$  and  $\text{L}^5$  each represents an optionally substituted methine group, and  $m$  is 0 or 1.

6. A photosensitive composition as claimed in Claim 1, 2 or 3, wherein the sensitizing dye has the general formula:



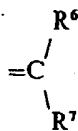
wherein  $\text{Z}^5$  represents the atoms needed to form a benzene ring or naphthalene ring,  $\text{R}^4$  and  $\text{R}^5$  are each optionally substituted alkyl groups or aryl groups,  $\text{W}$  represents a divalent group and  $n$  is 0, 1 or 2.

7. A photosensitive composition as claimed in Claim 4, wherein  $\text{Z}^1$  and  $\text{Z}^2$  are each selected from oxazole, naphthoxazole, thiazole, benzthiazole, selenazole, naphthoselenazole, imidazole, benzimidazole, naphthoimidazole, pyridine, indolenine and quinoline nuclei, which may be substituted.

8. A photosensitive composition as claimed in Claim 4, 5 or 6, wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$  and  $\text{R}^5$  are selected from alkyl, carboxyalkyl, sulphonyl, sulphonylalkoxy, aminoalkyl, benzalkyl, cyanoalkyl, allyl groups, and aryl groups containing a benzene ring.

9. A photosensitive composition as claimed in Claim 6, wherein  $\text{W}$  is the group  $=\text{N}$ -aryl wherein the aryl moiety contains a benzene ring.

10. A photosensitive composition as claimed in Claim 6, wherein  $\text{W}$  is the group



wherein  $\text{R}^6$  and  $\text{R}^7$  is each a cyano group, alkyl carbonyl group or alkoxy carbonyl group wherein the alkyl moiety has 1 to 4 carbon atoms, 5- or 6-membered nitrogen-containing heterocyclic nucleus, benzene-containing aryl group or cyano group.



11. A photosensitive composition as claimed in any preceding claim, wherein the dye has a maximum reduction potential of 3.00 volts.
12. A photosensitive composition as claimed in any preceding claim, wherein the dye is any of 27 dyes designated I to XXVII of the formulae shown hereinbefore.
13. A photosensitive composition as claimed in any preceding claim, wherein the sensitizing dye is present in an amount of  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  mole per mole of silver halide.
14. A photosensitive composition as claimed in any preceding claim, wherein the halide contains at least 40 mole % of silver iodide.
15. A photosensitive composition as claimed in any of Claims 1 to 14, in the form of a photographic silver halide emulsion.
16. A photographic emulsion as claimed in Claim 15 wherein the silver halide grains have a diameter of 0.005 to 0.8 micron.
17. A photographic emulsion as claimed in Claim 15 or 16, wherein the emulsion also contains a compound of a metal of Group Ib, IIb, III, V or VIII of the Periodic Table.
18. A photographic emulsion as claimed in Claim 17, wherein the metal compound is present in an amount of  $10^{-7}$  to  $10^{-3}$  moles per mole of silver of the silver halide.
19. A photographic emulsion as claimed in any of Claims 15 to 17, wherein the silver halide is held in a binder which serves as a protective colloid and which is gelatin, a derivative of gelatin, or a water-soluble synthetic polymer.
20. A photographic emulsion as claimed in any preceding claim, which has been prepared substantially as hereinbefore described in Preparation Example 1 or 2.
21. A photographic emulsion as claimed in Claim 15, substantially as hereinbefore described with reference to any of the samples of Examples 1 to 3 wherein Dye I is used.
22. A photographic emulsion as claimed in any of Claims 15 to 21 wherein the sensitizing dye has been added directly to the silver halide emulsion.
23. A photographic emulsion as claimed in any of Claims 15 to 22 wherein the sensitizing dye has been added to the emulsion whilst dissolved in an organic solvent together with a proton donor or a metal ion.
24. A photographic emulsion as claimed in any of Claims 15 to 21 wherein the sensitizing dye has been added to the emulsion in the form of globules of a solution in an oily solvent.
25. A photographic element which comprises a layer of a photosensitive silver halide emulsion as claimed in any of Claims 15 to 24 coated on a support.
26. A heat-developable photosensitive material comprising, coated on a support, a layer of (1) an organic silver salt, (2) a light-sensitive silver halide as defined in Claim 1, (3) a reducing agent and (4) a sensitizing dye as defined in any of Claims 1 to 13.
27. A heat-developable material as claimed in Claim 26, wherein the organic silver salt (1) is a silver salt of an organic carboxylic acid or of a heterocyclic compound containing a mercapto or imino group.
28. A heat-developable material as claimed in Claim 27 or 28, wherein the salt is a silver salt of an aliphatic carboxylic acid having more than 10 carbon atoms in the chain.
29. A heat-developable light-sensitive material as claimed in Claim 27 or 28, wherein the organic silver salt is a silver salt of benzotriazole, saccharin or phthalazinone.
30. A heat-developable light-sensitive material as claimed in any of Claims 25 to 29, wherein the silver halide (2) has been prepared by reacting in the composition the organic silver salt (1) with an organic or inorganic halide.
31. A heat-developable light-sensitive material as claimed in Claim 30, wherein the reaction is with an inorganic halide of the formula  $MX_n$ , where X is halogen at least 30 mole % of which is iodide,  $n$  is the valence of M, and M is hydrogen, ammonium or a metal.
32. A heat-developable light-sensitive material as claimed in any of Claims 26 to 31, wherein the amount of organic silver salt calculated as silver per square metre of support is from 0.2 to 3 grams.
33. A heat-developable light-sensitive material as claimed in any of Claims 26 to 32, wherein the silver halide or halide present for forming the silver halide is present in an amount of from 0.001 mole to 0.5 mole per mole of the organic silver salt, the reducing agent is present in an amount of from 0.01 mole to 5 moles per

mole of the organic silver salt, and the weight ratio of binder to organic silver salt is 4:1 to 1:4.

34. A heat-developable light-sensitive material as claimed in any of Claims 26 to 33, wherein said layer is overcoated with a polymer which withstands to temperatures above 115°F, is colourless and is soluble in an organic solvent used to form the overcoating layer.

35. A heat-developable light-sensitive material as claimed in Claim 26, substantially as hereinbefore described with reference to any of the samples of Examples 4 to 6, wherein one of Dyes I to XXVII is used.

36. A process for forming a photograph which comprises imagewise exposing a photographic element as claimed in Claim 25 and developing the exposed element in a silver halide developer.

37. A process for forming a visible image, which comprises imagewise exposing a photosensitive material as claimed in any of Claims 26 to 35 and heating the exposed material at a temperature of 100° to 160° until a visible image is obtained.

38. Sheets bearing visible images formed by the process of Claim 36 or 37.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1976.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.

1422057

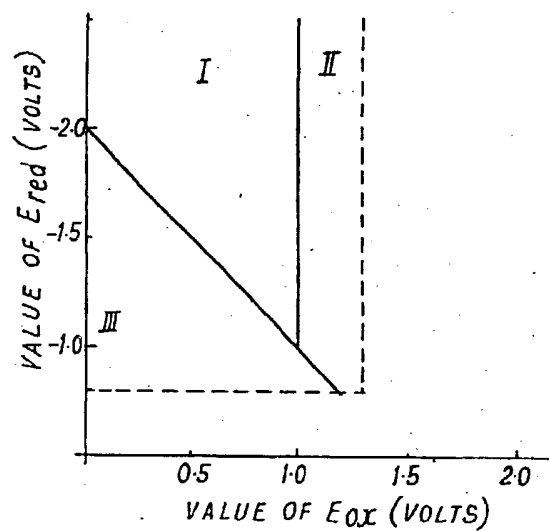
COMPLETE SPECIFICATION

3 SHEETS

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the Original on a reduced scale

Sheet 1

FIG. 1



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Sheet 2

